

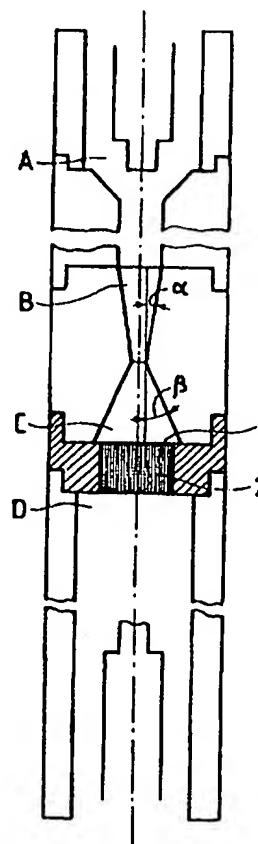


INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶: C01B 3/38, B01J 8/00, 8/02	A1	(11) International Publication Number: WO 97/37929 (43) International Publication Date: 16 October 1997 (16.10.97)
(21) International Application Number: PCT/EP97/01803 (22) International Filing Date: 8 April 1997 (08.04.97) (30) Priority Data: MI96A000690 11 April 1996 (11.04.96) IT (71) Applicant (for all designated States except US): SNAMPRO-GETTI S.p.A. [IT/IT]; Viale De Gasperi, 16, I-20099 San Donato Milanese (IT). (72) Inventors; and (75) Inventors/Applicants (for US only): BASINI, Luca [IT/IT]; Via Stradella, 7, I-20129 Milano (IT). DONATI, Gianni [IT/IT]; Via Meda, 30, I-20017 Rho (IT). (74) Agents: FUSINA, Gerolamo et al.; Ing. Barzano' & Zanardo Milano S.p.A., Via Borgonuovo, 10, I-20121 Milano (IT).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>

(54) Title: EQUIPMENT FOR PARTIAL OXIDATION REACTIONS**(57) Abstract**

Equipment for carrying out partial oxidation reactions characterized in that it essentially comprises four operating zones: a feeding zone (A); a distribution zone (B) with a constant or decreasing section along the axis of the equipment in the direction of the gas propagation, preferably in the form of a cylindrical, truncated-conical or truncated-pyramidal solid, consisting of one or more parts of said solid, optionally substituted by their external or internal envelope curved surface, wherein the angle (α) of the generatrix with the vertical parallel to said axis is between 0 and 65°; a reaction zone (C), consisting of a catalytic bed, with an increasing section along the axis of the equipment in the direction of the gas propagation, communicating with said distribution zone by means of a common transversal section, preferably in the form of a truncated-conical or truncated-pyramidal solid, consisting of one or more parts of said solid, optionally substituted by their external or internal envelope curve surface, in which the angle (β) of the generatrix with the vertical parallel to said axis is between 5 and 65°; a gas expansion zone (D).



FOR THE PURPOSES OF INFORMATION ONLY

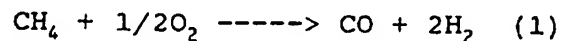
Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakhstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

EQUIPMENT FOR PARTIAL OXIDATION REACTIONS

The present invention relates to equipment for carrying out partial oxidation by means of a suitable catalyst.

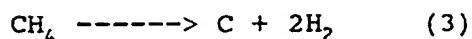
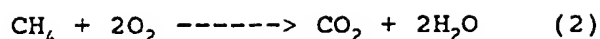
5 In particular this equipment can be used for producing synthesis gas by the partial oxidation of natural gas in the presence of oxygen and/or air by the reaction



10 On an industrial scale, the partial oxidation of natural gas is carried out with two types of technological solutions.

In the first type of technological solution non-catalytic reactors are used in which the reaction gases
15 are mixed in a water-cooled burner and react in a combustion chamber ($T=1300-1500^\circ\text{C}$) lined with refractory materials. In this process the partial oxidation reactions (OP) (1) compete with the following total oxidation reactions (2) and with the cracking reactions

(3):

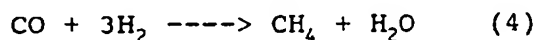


In addition, the sub-stoichiometric combustion
5 reactions cause radicalic dehydrogenation reactions of
the molecules with two or more carbon atoms and the
formation of ethylene and/or acetylene compounds. These
in turn can be precursors of carbonaceous residues.

The reaction products enter at 1400°C into an
10 exchanger whose design and functioning are complicated
by the combination of factors relating to the high
temperature and presence of carbonaceous residues. To
eliminate the carbonaceous residues from the products
the synthesis gas is washed with water.

15 The selectivity and conversions depend on various
factors among which the most important are:

- design of the burner;
- the ratio O_2/C (oxygen moles/carbon atom moles) in the
mixture of the reagents;
- 20 - reduced residence time inside the reactor;
- the rapid cooling of the reaction products which at
intermediate temperatures (700-400°C) can recombine
to reform methane and H_2O by means of the reaction

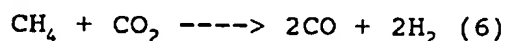
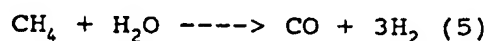


25 In the second type of technological solution

autothermal catalytic reactors are used.

In this process the streams of the preheated reagents are mixed at 500-650°C in a burner situated at the inlet of the reactor, generating a turbulent flame
5 which spreads to a combustion chamber situated between the burner and an underlying catalytic bed.

The sub-stoichiometric combustion reactions use up part of the natural gas and produce mixtures of carbon monoxides and steam as well as the heat necessary for
10 the following reforming strongly endothermic reactions of steam (5) and CO₂ (6):



The latter take place in a catalytic bed beneath
15 the combustion chamber filled with a catalyst based on Ni (15-30% by weight deposited on spinels of aluminium and magnesium oxides with a high thermal resistance). These reactors operate at a GHSV which is typically between 5000-10000 NL/(Lcat x h) and in any case not
20 higher than 15000 NL/(Lcat x h).

As already mentioned, in the case of non-catalytic processes the synthesis gas produced must be purified by washing with water. In autothermal reactors on the other hand the unsaturated molecules and carbonaceous
25 residues are decomposed in the catalytic bed making the

washing of the gas useless; also the temperatures leaving the reactor are lower (typically 950°C). These characteristics simplify the characteristics of the exchangers for the thermal recovery of the gas leaving
5 the reactor and improve the thermal efficiency of the process.

Several patent applications have recently been published (WO-95/18062; EP-576096; EP-629578) which claim catalytic processes carried out at a high temper-
10 ature ($T > 950^{\circ}\text{C}$) and also high pressure ($P = 1\text{--}150$ Bars) in tubular reactors with a GHSV of between 20,000 and 20,000,000 NL/(Lcat x h).

In experiments carried out in our laboratories it has been found that the conditions of high temperature
15 and high pressure claimed in these patents are difficult to apply at pressures greater than 10 atm and temperatures higher than 950°C as, under the fluid-dynamic conditions described, the mixtures of the reagents and products ignite in gaseous phase causing the
20 total combustion of the hydrocarbons with losses in selectivity towards CO and H₂ and the formation of carbon black which rapidly blocks the catalytic bed.

In a recent patent application of the same applicant (EP-640559) integrated processes of catalytic
25 partial oxidation are claimed for the production of CO

and H₂ and the synthesis of methanol, dimethylether and FT, in which formaldehyde is also produced, carried out at temperatures of between 300 and 950°C, pressures of between 1 and 40 atms and a GHSV of between 20,000 and
5 1,500,000 NL/(L cat x h).

Also in this process, in which the operating conditions are less drastic than the three patents cited above, from which it also differs in the possibility of carrying out the reactions with O₂/CH₄ ratios
10 > 0.5 (v/v), the process conditions are difficult to apply for the same reasons specified above when the pressures exceed 15 atms.

A catalytic reactor has now been found which improves the quality of the process claimed in the
15 above application of the same applicant, capable of carrying out partial oxidation reactions which, apart from having considerably reduced dimensions with respect to those used in commercial processes, does not require the presence of a burner and enables partial
20 oxidation catalytic reactions to be carried out maintaining the mixtures of reagents at rates higher than flame speed and avoiding drops in pressure due to expansion of the gaseous reaction mixture.

The equipment which is the main object of the
25 present invention, is characterized in that it compris-

es four operating zones:

- a feeding zone (A);
- a distribution zone (B) with a constant or decreasing section along the axis of the equipment
5 in the direction of the gas propagation;
- a reaction zone (C), consisting of a catalytic bed, with an increasing section along the axis of the equipment in the direction of the gas propagation, communicating with said distribution zone by
10 means of a common transversal section;
- a gas expansion zone (D).

The distribution zone (B) is preferably in the form of a cylindrical, truncated-conical or truncated-pyramidal solid, consisting of one or more parts of
15 said solid, optionally substituted by their external or internal envelope curved surface, wherein the angle (α) of the generatrix with the vertical, parallel to said axis, is between 0 and 65°, more preferably between 10 and 45°.

20 The reaction zone (C) is preferably in the form of a truncated-conical or truncated-pyramidal solid, consisting of one or more parts of said solid, optionally substituted by their external or internal envelope curve surface, wherein the angle (β) of the generatrix
25 with the vertical parallel to said axis is between 5

and 65°, more preferably between 10 and 45°.

The functions of the distribution zone are the following:

- to act as propagation barrier of the radicalic reactions towards the feeding inlet, both by acceleration of the fluid and by the presence of inert surfaces, capable of capturing the radicals;
- to distribute the fluid uniformly on the transversal section common to the two distribution and reaction zones.

The functions of the reaction zone are:

- to activate the reaction in the section where there is the highest gas velocity;
- to follow the expansion of the fluid due to an increase in the number of moles and temperature without the inconveniences caused by high losses in the charge;
- maintain a surface rate in the whole bed higher than the critical value which causes the production of flame and carbon black.

The fluid-dynamic conditions inside the reaction zone must be such as to avoid overheating of the reaction mixture but also drops in pressure in the direction of the gas propagation. The drop in pressure is caused by the rapid increase in the volume of the

gaseous mixture in correspondence with the necking inside the catalytic zone. The stagnation of the reagent mixture upstream of the necking causes its overheating and ignition and must therefore be avoided.

5 The variation in the diameter of the reaction zone and the consequent decrease in the gas velocity reduces the effect of the drop in pressure. A differential filling of the catalytic bed with particles with an increasing diameter along the gas propagation direction
10 contributes to reducing the drop in pressure.

The equipment of the present invention can have cooling systems both in the feeding zone and/or in the post-reaction zone and in the distribution and/or reaction zone.

15 The partial oxidation process with the catalytic autothermal reactor described above, which forms a second object of the present invention, basically consists in the following steps:

- premixing and, upon activation, preheating to
20 temperatures of between 200 and 600°C, below flammability values, the reagents consisting of natural gas, oxygen or air or air enriched with oxygen, optionally steam and/or CO₂, so that the surface velocity of the reaction gases is main-
25 tained above the flame speed and the temperature

of the reagent mixture in the zone preceding the catalytic bed is below its flammability temperature;

- reacting by interaction of the catalysts the mixture of reagents in the reaction zone, the reaction being activated at temperatures of between 200 and 600°C and carried out at space velocities of between 10,000 and 10,000,000 NL reagents/L cat x h, more preferably between 100,000 and 5,000,000, reaching temperatures of between 700 and 1350°C.

The limits of the first step are necessary for avoiding the creation of uncontrolled combustion phenomena in gaseous homogeneous phase in the zone preceding or inside the catalytic bed. These reactions reduce the selectivity towards the production of synthesis gases, cause the formation of carbonaceous residues which deactivate the catalyst and when there is nitrogen in the reagent mixture, they also cause the formation of nitrogen oxides (NO_x).

The preferred ratios between the reagents in the reaction mixture consisting of natural gas, air or air enriched with oxygen, possibly steam and/or CO_2 , are the following:

- ratio between steam moles/moles of hydrocarbon
q

carbon atoms (steam/C) of between 0 and 3.5, more preferably between 0.1 and 1.5;

- ratio molecular oxygen moles/moles of hydrocarbon carbon atoms (O_2/C) of between 0.15 and 0.7, more preferably between 0.4 and 0.6.

The use of these space velocities allows very low quantities of catalyst to be consumed and high productivities to be obtained which easily exceed values of about $200,000 \text{ m}^3 \text{ CO} + \text{H}_2/\text{day} \times \text{kg catalyst}$, i.e. twice as higher than those obtained with the known processes for the production of synthesis gases.

The presence of steam and CO_2 as well as other molecules more chemically inert, such as nitrogen, changes the flammability point of the gaseous reagent mixtures, enabling the geometry to be varied in the reaction zone and higher pressures to be applied with lower surface velocities.

In the reactor adopted in the process, catalysts are preferably used in which one or more noble metals (Rh, Ru, Ir, Pd, Pt, etc.) and/or Ni are deposited on a carrier consisting of a material capable of supporting considerable thermal and mechanical stress (typically SiC , $\text{Mg}_x\text{Al}_y\text{O}_z$, $\alpha\text{-Al}_2\text{O}_3$, ZrO_2 , yttrium stabilized with zirconium). The catalysts are prepared by anchoring the noble metals (preferably Rh, Ru, Ir) and/or Ni

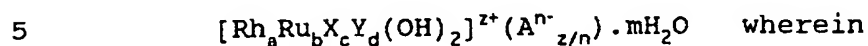
in percentages of between 0.05 and 15% by weight, preferably between 0.1 and 5% by weight, onto the carriers. This operation is carried out with three methods.

5 A first method is carried out by solid-liquid reactions, by interaction between the carriers dispersed in an organic solvent and solutions of clusters of noble metals (such as $\text{Rh}_4(\text{CO})_{12}$, $\text{Rh}_6(\text{CO})_{16}$, $\text{Ru}_3(\text{CO})_{12}$, $\text{Ir}_4(\text{CO})_{12}$;

10 A second method is carried out by impregnation of the solid carriers with water solutions of inorganic salts of noble metals (such as RhCl_3 , $\text{Rh}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$, $\text{Ru}(\text{NO})(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$, $\text{NiNO}_3 \cdot x\text{H}_2\text{O}$).

 The method which comprises the use of small
15 carbonyl clusters of noble metals enables the production of particularly active catalysts, capable of activating partial oxidation reactions at lower temperatures (typically 250°C). The method comprising the use of inorganic salts of noble metals leads to the
20 production of catalytic materials capable of activating combustion reactions only at temperatures higher than 350°C . In both cases however the activating temperatures are much lower than those used in the burners of non-catalytic reactors or catalytic autothermal reac-
25 tors.

A third method for preparing the catalysts involves the synthesis of an intermediate of the hydrotalcite type, described in patent application IT-Mi95A00184, represented with the formula:



X is a bivalent or monovalent metal cation

Y is a trivalent or tetravalent metal cation

$$0 \leq a \leq 0.5, \quad 0 \leq b \leq 0.5, \quad 0.5 \leq c \leq 0.9,$$

$$0 \leq d \leq 0.5, \quad a + b + c + d = 1,$$

10 m is equal to zero or a positive number,

A can be a hydroxyl, any inorganic, organic anion, iso or heteropolyanion, anionic complex or organo-metallic complex, having n charge,

z is the total charge of the cationic component.

15 The atomic ratios between the elements are preferably within the following ranges:

$$0 \leq a \leq 0.33, \quad 0 \leq b \leq 0.33, \quad 0.66 \leq c \leq 0.8,$$

$$0 \leq d \leq 0.33.$$

The bivalent metal cation X is preferably selected
 20 from Mg, Ni, Co, Zn, Fe, Mn, Cu, Ca and Cd. The monovalent metal cation X is preferably lithium. The trivalent metal cation Y is preferably selected from Al, Ga, Ni, Co, Fe, Mn, Cr, V, Ti and In. The tetravalent metal cation Y is preferably titanium.

25 The hydrotalcite intermediate is subjected to a

thermal treatment at temperatures higher than 700°C before being used in the catalytic reactions.

The preparation of the hydrotalcite material described above can be carried out as described in 5 "Catalysis Today", 11, 173 (1991) (F.Cavani, F.Trifirò and A.Vaccari) and in "Expanded Clays and Other Microporous Solids", (A de Roy, C.Forano, K.El Malki and J.P.Besse) Ed., M.L.Occelli and H.E.Robson, Vol.2, Reinhold, New York, 1992, page 108).

10 In particular the hydrotalcite catalytic materials can be prepared using a water solution containing in suitable proportions the salts of rhodium and/or ruthenium, a bivalent or monovalent element and another trivalent or also tetravalent element. This solution is 15 added under vigorous stirring and at a temperature of between 30 and 90°C, and preferably between 50 and 70°C, to a solution of alkaline carbonate or bicarbonate, care being taken, also by the additional addition of acids or bases, that the pH be maintained during the 20 precipitation at a constant value within the range of 7-12 and preferably 8-11. In this way there is the contemporaneous precipitation of all the elements and their fine interdispersion. The crystalline precipitate formed is separated and washed with water, preferably 25 hot, until there is a content of alkaline expressed as

oxide of less than 0.1%. The precipitate is subsequently dried at 100°C and calcined in air or nitrogen at a temperature of between 200 and 1100°C, preferably between 350 and 950°C.

5 To come back to the composition of the catalysts both rhodium and ruthenium can be used contemporaneously or rhodium and nickel, the rhodium being used in a first layer of the catalytic bed and the ruthenium or nickel in a second layer of the bed underneath the
10 first.

In this case the catalytic bed containing rhodium is preferably between 20 and 35% by volume of the whole catalytic bed.

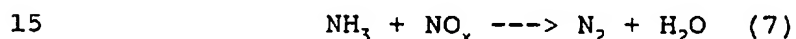
With this configuration, it is possible to reduce,
15 if necessary owing to lack of availability and/or high costs, the use of rhodium in the whole catalytic bed, by completely substituting it with ruthenium or with nickel and using compositions of the charge and reaction conditions which are less favourable to cracking
20 reactions of the hydrocarbons.

With respect to the catalytic bed, it is advisable to fill this with catalyst having an increasing average particle diameter along the direction of the gas propagation so as to increase the vacuum degree and
25 reduce losses of the charge.

A particular advantage of the catalytic reactor described above and consequently of the processes in which it is used, consists in enabling the production of synthesis gases using mixtures containing air or air
5 enriched with oxygen reducing the formation of NO_x .

This surprising advantage allows the partial oxidation catalytic reactor to be used both for the production of CO and H_2 for chemical use and for the generation of electric energy with gas turbines thus
10 avoiding polluting effects due to the production of NO_x .

At present pollution due to the production of NO_x is reduced by the use of selective reduction processes in the presence of ammonia whose chemistry is synthetically represented by the equation:



An embodiment of the invention is provided with the help of fig. 1, but this should not be considered as limiting the scope of the invention.

The equipment consists of a first feeding zone
20 (A), followed by a distribution zone (B), with a decreasing section, in the form of a truncated cone, having the α angle of the generatrix with the vertical equal to 25° , followed by a reaction zone (C), having the circle-shaped section (1) in common with the
25 previous zone, with an increasing section, in the form

of a truncated cone, having the β angle of the generatrix with the vertical equal to 35° , followed by an expansion zone (D) consisting of a honeycomb carrier (2) and a wider chamber.

- 5 The following examples provide a better illustration of both the catalytic reactor and the process claimed.

Example 1 - Comparative

Refractory alumina cylinders shaped so as to be
10 able to contain a conventional cylindrical catalytic bed (diameter 15 mm, height 20 mm, weight 1 g) are introduced into a cylindrical steel reactor having a thickness of 1 cm and an internal diameter of 5 cm. The catalyst was obtained using as carrier a foamy ceramic
15 monolith in $\alpha\text{-Al}_2\text{O}_3$ with a porosity of 30 pores per inch (ppi), containing 3% by weight of Ru. The noble metal was deposited by dripping a water solution of $\text{Ru}(\text{NO})(\text{NO}_3) \cdot x\text{H}_2\text{O}$ onto the monolith; the monolith was subsequently calcined for 4 h at a temperature of
20 550°C, to decompose the ruthenium salts. The metal of the carrier was subjected to thermal treatment in an atmosphere of $\text{H}_2/\text{N}_2 = 1/1$ (v/v) at 600°C for 8 hours before the beginning of the catalytic test.

The test was carried out at a pressure of 6 atm.,
25 air cooling helped to maintain the temperature of the

reagents at the inlet at less than 300°C. A series of thermocouples, inserted in two sheaths, the internal one made of steel and the external one of quartz, situated along the longitudinal section of the reactor, enabled the temperature to be monitored in different positions and in particular at the inlet and outlet of the catalytic bed (at 5 and 9 mm therefrom respectively). The mixture of outgoing products is cooled with a ceramic water exchanger. The duration of the catalytic test was 100 h. In this test the feeding (1000 Nl/h) consisted of a mixture of CH₄, O₂ and H₂O in a ratio of 2/1/1.

The operating conditions and results are summarized in table 1.

At pressures higher than 8.5 atms. the cylindrical reactor no longer enabled the operating parameters to be correctly handled owing to the uncontrolled formation of flame reactions and an increase in the loss values of the charge.

Examples 2-5

Refractory alumina cylinders shaped so as to be able to form a gas distribution zone and an sandglass-shaped catalytic bed as schematized in fig. 2, are introduced into a cylindrical steel reactor having a thickness of 1 cm and an internal diameter of 5 cm.

The equipment consists of:

- a first feeding zone (A) into which the reagents are charged, equipped with a cooling system using a suitable fluid (F);
- 5 - a distribution zone (B), with a decreasing section, in the form of a truncated cone, having the α angle of the generatrix with the vertical equal to 20° on the outside of which is a cooling system;
- 10 - a reaction zone (C), having the circle-shaped section (1) in common with the previous zone, with an increasing section, in the form of a truncated cone, having the β angle of the generatrix with the vertical equal to 30° , on the outside of which
15 is a cooling system;
- a post-reaction zone consisting of a honeycomb carrier (2) and a wider chamber equipped with a cooling system.

The distribution system of the reagent mixture was
20 obtained using alumina spherical particles ($d = 1.5-2$ mm), calcined for 4 h at 1020°C . The distributor has a diameter at the inlet (r_i) of 15 mm, a diameter at the outlet (r_f) of 5 mm and a length (L) of 20 mm. The catalytic bed (2.45 g) was formed using the same
25 alumina particles used in the distributor, containing

0.5% of Rh. The noble metal was deposited on the alumina by contact with a solution of $\text{Rh}_4(\text{CO})_{12}$ in n-hexane. After drying the catalyst was charged into the reactor and used in reaction without any activation treatment. The dimensions of the reaction zone are the following:

$$r_i = 5 \text{ mm}; r_f = 25 \text{ mm}; L = 20 \text{ mm}.$$

As a support for the spherical particles of catalyst a porous ceramic monolithic disk was used, with 40 ppi, in alumina (diameter 40 mm and thickness 20 mm).

The test was carried out at a pressure of 10 atms. The thermocouples for monitoring the temperature at the inlet and outlet of the catalytic bed were positioned at a distance of 25 and 27 mm respectively. The duration of the catalytic test was 20 h. The pressure loss was equal to about 0.2 atms. In these examples CH_4 and O_2 were fed with volumetric ratios CH_4/O_2 varying from 2.4 to 6. During the catalytic tests the temperature of the gas at the inlet of the distribution zone was maintained at between 250 and 300°C.

The results obtained are shown in table 2.

Example 6

The same experimental conditions were applied as in examples 2-5 with the same catalyst, but feeding in

addition to CH_4 and O_2 , also CO_2 in the ratio of 8:4:1.

The results obtained are shown in table 2.

Examples 7-9

In this case the distribution zone has a diameter
5 at the inlet (r_i) of 15 mm, a diameter at the outlet
(r_f) of 5 mm and a length (L) of 20 mm, whereas the
catalytic reaction zone is characterized by an r_i of 5
mm, an r_f of 33mm and a length equal to 30 mm.

The catalyst is obtained using the same alumina
10 spherical particles described in examples 2-6 but with
an increasing diameter of between 1.5 and 5 mm. As a
support for the catalyst a porous ceramic monolithic
zirconia disk was used (40 ppi), having a diameter of
40 mm and a thickness of 20 mm. The catalytic test was
15 carried out at a pressure of 17 atms. To increase the
thermal exchange and reduce the temperatures at the
inlet an air-cooling circuit was used consisting of a
copper perforated tube, ring-shaped and positioned
around the core of the reactor. The thermocouples for
20 monitoring the temperature at the inlet and outlet of
the catalytic bed were positioned in both cases at a
distance of 25 mm. In example 7 a reagent mixture
consisting of CH_4 , O_2 was fed in a ratio of 3:1. In
example 9 a reagent mixture consisting of CH_4 , O_2 and
25 CO_2 was fed in a ratio of 4:2:1. The remaining experi-

mental conditions are the same as in example 1. The operating conditions and results of the catalytic tests described in examples 7, 8 and 9 are schematized in table 3.

Table 1

		<u>Ex. 1</u>
	P (atm)	6
5	GHSV (h^{-1})	1000000
	CH_4/O_2	2
	$T_{\text{in cat}}$ ($^{\circ}\text{C}$)	502
	$T_{\text{out cat}}$ ($^{\circ}\text{C}$)	878
	$v_{\text{gas in}}$ (m/s)	0.87
10	$v_{\text{gas out}}$ (m/s)	2.39
	% Convers. CH_4	92.7
	% Convers. O_2	100
	% Select. CO	92.7
	% Select. H_2	98.6
15	CH_4 % (gas out)	1.9
	O_2 % (" ")	0
	CO % (" ")	22.6
	H_2 % (" ")	48.4
	CO_2 % (" ")	5.1
20	H_2O % (" ")	21.9

(Selectivities to CO and H_2 are calculated on the basis of the conversion of CH_4)

Table 2

		Ex. 2	Ex.3	Ex.4	Ex.5	Ex.6
5	P (atm)	10	10	10	10	10
	GHSV (h ⁻¹)	381220	408160	434690	464080	530610
	CH ₄ /O ₂	6	4	3	2.4	2
	T _{in} cat(°C)	346	263	259	264	362
	T _{out} cat(°C)	625	662	704	714	762
10	v gas _{in} (m/s)	4.15	2.98	3.14	3.41	4.28
	v gas _{out} (m/s)	0.45	0.32	0.36	0.44	0.56
	% Convers. CH ₄	27.4	36.1	48.8	49.1	75.5
	% Convers. O ₂	100	100	100	100	100
	% Select. CO	81.8	85.1	84.5	83.8	99.7
15	% Select. H ₂	84.5	91.0	86.4	81.0	86.0
	CH ₄ % (gas out)	47.4	37.4	26.3	25.9	9.3
	O ₂ % (" ")	0	0	0	0	0
	CO % (" ")	14.7	17.9	21.1	20.9	28.5
	H ₂ % (" ")	30.3	38.3	43.3	40.4	49.2
20	CO ₂ % (" ")	2.7	2.5	2.2	1.9	4.6
	H ₂ O % (" ")	4.9	3.8	7.1	10.9	8.4

(Selectivities to CO and H₂ are calculated on the basis of the conversion of CH₄).

Table 3

=====				
	Ex. 7	Ex.8	Ex.9	

5	P (atm)	17	17	17
	GHSV (h ⁻¹)	164180	158960	208955
	CH ₄ /O ₂	4	3	2
	T _{in} cat (°C)	372	273	372
	T _{out} cat (°C)	641	619	788
10	v gas _{in} (m/s)	2.53	2.08	3.21
	v gas _{out} (m/s)	0.14	0.14	0.27
	% Convers. CH ₄	31.4	43.7	88.7
	% Convers. O ₂	100	100	100
	% Select. CO	90.4	85.7	90.8
15	% Select. H ₂	74.5	79.3	69.1
	CH ₄ % (gas out)	40.5	30.2	4.6
	O ₂ % (" ")	0	0	0
	CO % (" ")	16.8	20.1	32.8
	H ₂ % (" ")	27.7	37.2	49.9
20	CO ₂ % (" ")	5.8	2.9	3.8
	H ₂ O % (" ")	9.3	9.7	8.9

=====

(Selectivities to CO and H₂ are calculated on the basis of the conversion of CH₄).

CLAIMS

- 1) Equipment for carrying out partial oxidations characterized in that it essentially comprises four operating zones:
- 5 - a feeding zone (A);
- a distribution zone (B) with a constant or decreasing section along the axis of the equipment in the direction of the gas propagation;
- 10 - a reaction zone (C), consisting of a catalytic bed, with an increasing section along the axis of the equipment in the direction of the gas propagation, communicating with said distribution zone by means of a common transversal section;
- 15 - a gas expansion zone (D).
- 2) Equipment according to claim 1 wherein the distribution zone (B), with a constant or decreasing section, is in the form of a cylindrical, truncated-conical or truncated-pyramidal solid, consisting of one or more parts of said solid, optionally substituted by their external or internal envelope curved surface, wherein the angle (α) of the generatrix with the vertical, parallel to the axis
- 20 of said equipment, is between 0 and 65°,
- 25

and the reaction zone (C) with an increasing section, communicating with the distribution zone by means of a common transversal section, is in the form of a truncated-conical or truncated-pyramidal solid, consisting of one or more parts of said solid, optionally substituted by their external or internal envelope curve surface, wherein the angle (β) of the generatrix with the vertical, parallel to the axis of said equipment, is between 5 and 65°.

- 3) Equipment according to claim 2 wherein the angle α is between 10 and 45° and the angle β is between 10 and 45°.
- 4) Equipment according to claim 1 wherein the feeding zone is equipped with a cooling system of the reagents.
- 5) Equipment according to claim 1 wherein the expansion zone is equipped with a cooling system.
- 6) Equipment according to claim 1 wherein the distribution and/or reaction zone is equipped with a cooling system.
- 7) Process of partial oxidation with the use of the equipment according to any of the claims from 1 to 6 comprising the following steps:
 - premixing and, upon activation, preheating to

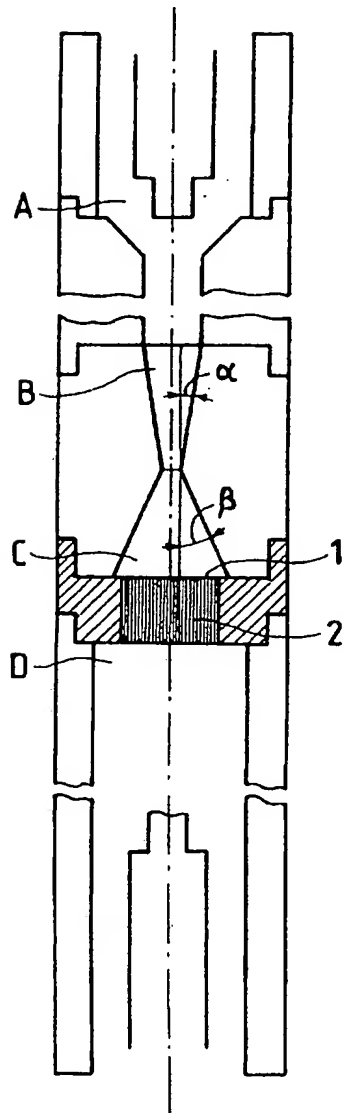
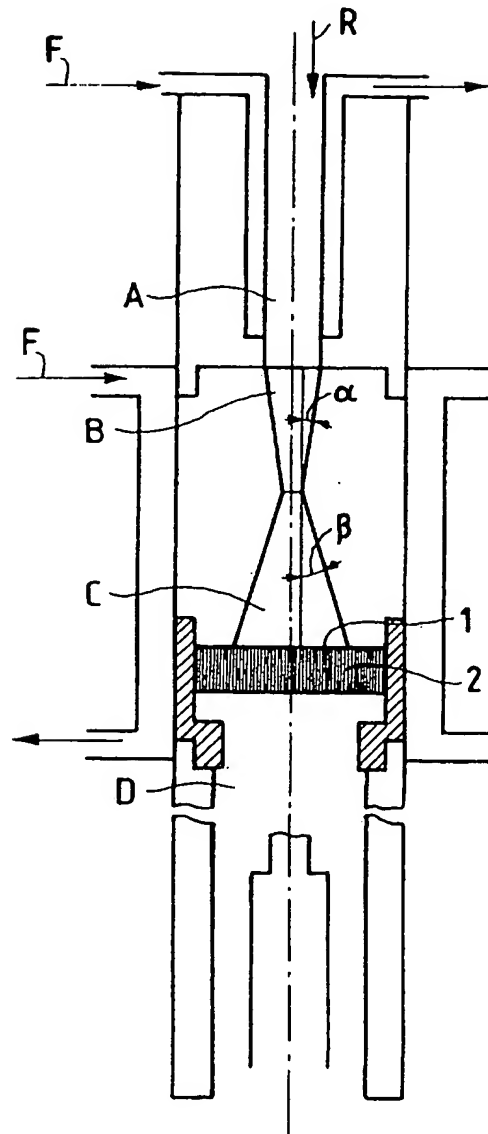
- temperatures of between 200 and 600°C, below flammability values, the reagents consisting of natural gas, oxygen or air or air enriched with oxygen, optionally steam and/or CO₂, so that the surface velocity of the reaction gases is maintained above the flame speed and the temperature of the reagent mixture in the zone preceding the catalytic bed is below its flammability temperature;
- 5
- 10 - reacting by interaction of the catalysts the mixture of reagents in the reaction zone, the reaction being activated at temperatures of between 200 and 600°C and carried out at space velocities of between 10,000 and
- 15 10,000,000 Nl reagents/L cat x h, reaching temperatures of between 700 and 1350°C.
- 8) Process according to claim 7 wherein the reaction is activated at temperatures of between 250 and 450°C, whereas the space velocities are between
- 20 100,000 and 5,000,000 Nl reagents/L cat x h.
- 9) Process according to claim 7 wherein, among the reagents, the ratio between steam moles/moles of hydrocarbon carbon atoms (steam/C) is between 0 and 3.5
- 25 and the ratio between molecular oxygen moles/

moles of hydrocarbon carbon atoms (O_2/C) is between 0.15 and 0.7.

- 10) Process according to claim 9 wherein the ratio between steam moles/moles of hydrocarbon carbon atoms (steam/C) is between 0.1 and 1.5 and the ratio between molecular oxygen moles/moles of hydrocarbon carbon atoms (O_2/C) is between 0.4 and 0.6.
- 11) Process according to claim 7 wherein the distribution zone of the equipment is filled with foamy monoliths and/or particles of ceramic material.
- 12) Process according to claim 9 wherein the porous ceramic material is selected from $\alpha-Al_2O_3$, $Al_xMg_yO_z$, ZrO_2 and SiC.
- 13) Process according to claim 7 wherein the catalyst consists of a compound of one or more noble metals and/or a compound of nickel deposited on a suitable carrier in a quantity of between 0.05 and 15% by weight.
- 14) Process according to claim 13 wherein the noble metals and/or nickel deposited on the carrier are in a quantity of between 0.1 and 5% by weight.
- 15) Process according to claim 13 wherein the noble metals are selected from rhodium, ruthenium, iridium, palladium and platinum.

- 16) Process according to claim 13 wherein the metals are rhodium and ruthenium or rhodium and nickel, the rhodium being used in a first layer of the catalytic bed and the ruthenium or nickel in a second layer of the bed underneath the first.
- 17) Process according to claim 16 wherein the catalytic bed containing rhodium is between 20 and 35% by volume of the whole catalytic bed.
- 18) Process according to claim 7 wherein the catalyst is a hydrotalcite intermediate, subjected to thermal treatment at temperatures higher than 700°C before being used in the catalytic reaction, having the following formula:
- $$[\text{Rh}_a\text{Ru}_b\text{X}_c\text{Y}_d(\text{OH})_2]^{z+}(\text{A}^{n-})_{z/n} \cdot m\text{H}_2\text{O} \quad \text{wherein}$$
- X is a bivalent or monovalent metal cation
- Y is a trivalent or tetravalent metal cation
- $$0 \leq a \leq 0.5, \quad 0 \leq b \leq 0.5, \quad 0.5 \leq c \leq 0.9,$$
- $$0 \leq d \leq 0.5, \quad a + b + c + d = 1,$$
- m is equal to zero or a positive number,
- A can be a hydroxyl, any inorganic, organic anion, iso or heteropolyanion, anionic complex or organo-metallic complex, having n charge,
- z is the total charge of the cationic component.
- 19) Process according to claim 7 wherein the catalytic bed is filled with catalyst having an increasing

average diameter of the particles along the direction of the gas propagation.

Fig.1Fig.2

INTERNATIONAL SEARCH REPORT

Internal Application No
PCT/EP 97/01803

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C01B3/38 B01J8/00 B01J8/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C01B B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 303 439 A (DAVY MCKEE CORP) 15 February 1989 see column 1, line 32 - column 2, line 3 see column 2, line 27 - column 3, line 20 see column 4, line 55 - column 5, line 3 see figures 1,2,5 ---	1-4,7
X	EP 0 303 438 A (DAVY MCKEE CORP) 15 February 1989 see column 3, line 33 - column 4, line 2 see column 6, line 46 - column 7, line 45 see column 9, line 48 - column 10, line 42 see figure 6; example ---	1,7-10, 13-15
A	DE 844 373 C (H. OSTWALD) 21 July 1952 see the whole document ---	1
	-/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

& document member of the same patent family

Date of the actual completion of the international search

10 July 1997

Date of mailing of the international search report

18.07.1997

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (- 31-70) 340-2040, Tx. 31 651 epo nl,
Fax (- 31-70) 340-3016

Authorized officer

Van der Poel, W

INTERNATIONAL SEARCH REPORT

Internat. J. Application No.

PCT/EP 97/01803

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 037 616 A (WILLIATTE CHRISTOPHE ET AL) 6 August 1991 see column 5, line 24 - column 6, line 42 see figures ---	1
A	EP 0 629 578 A (SHELL INT RESEARCH) 21 December 1994 cited in the application see page 3, line 51 - page 5, line 15 see examples ---	7-10, 13-15
P,X	EP 0 725 038 A (SNAMPROGETTI S.P.A) 7 August 1996 cited in the application see page 3, line 27 - line 42 see claims 13,14; example 9 -----	7,18

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 97/01803

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0303439 A	15-02-89	US 4865820 A	12-09-89
		AU 604956 B	03-01-91
		AU 2098888 A	16-02-89
		CA 1314129 A	09-03-93
		CN 1033753 A,B	12-07-89
		DE 3875305 A	19-11-92
		IN 171676 A	05-12-92
		JP 1159037 A	22-06-89
		KR 9609153 B	16-07-96
		SU 1711659 A	07-02-92

EP 0303438 A	15-02-89	AU 610219 B	16-05-91
		AU 2098988 A	16-02-89
		CN 1031511 A,B	08-03-89
		IN 171834 A	23-01-93
		JP 1145301 A	07-06-89
		SU 1831468 A	30-07-93

DE 844373 C		NONE	

US 5037616 A	06-08-91	FR 2621833 A	21-04-89
		CA 1336587 A	08-08-95
		CN 1033641 A,B	05-07-89
		EP 0312428 A	19-04-89
		IN 170034 A	01-02-92
		JP 1207388 A	21-08-89

EP 0629578 A	21-12-94	AU 672901 B	17-10-96
		AU 6478694 A	22-12-94
		BR 9402445 A	24-01-95
		CA 2126036 A	19-12-94
		CN 1101891 A	26-04-95
		JP 7010503 A	13-01-95
		NO 942284 A	19-12-94
		NZ 260621 A	26-03-96
		ZA 9404286 A	10-02-95

EP 725038 A	07-08-96	IT MI950184 A	05-08-96
